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"Toward Colloidal Dispersions of Template Synthesized Polypyrrole
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by Silvia De Vito and Charles R. Martin

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Colorado State University
Department of Chemistry
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13. Abstract: A procedure for preparing colloidal dispersions of template-synthesized polypyrrole nanotubules is described. This procedure entails the use of an anionic surfactant as a dispersing agent, and slow dissolution of the template membrane is critical. Dispersion of nominally 200 nm and 50 nm diameter polypyrrole nanotubules have been prepared.
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Toward Colloidal Dispersions of Template Synthesized Polypyrrole Nanotubules

Silvia De Vito, and Charles R. Martin*

Department of Chemistry, Colorado State University
Fort Collins, CO 80523 (USA)

* Corresponding author via E-mail at crmartin@lamar.colostate.edu

Abstract

A procedure for preparing colloidal dispersions of template-synthesized polypyrrole nanotubules is described. This procedure entails the use of an anionic surfactant as a dispersing agent, and slow dissolution of the template membrane is critical. Dispersion of nominally 200 nm and 50 nm diameter polypyrrole nanotubules have been prepared.

We and others have shown that monodisperse nanowires and tubules of electronically conductive polymers can be prepared by synthesizing the desired polymer within the pores of microporous filtration membranes (see (1,2) and references therein). The membranes employed contain cylindrical pores with monodisperse diameters, so that cylindrical nanowires or tubules with analogous monodisperse diameters are obtained. One of the advantages of this "template" (1,2) approach for preparing such cylindrical nanoparticles is that each particle is synthesized within its own pore and is thus isolated from neighboring particles. This prevents aggregation of the nanoparticles.

For some applications, it might be desirable to dissolve the template membrane and free the template-synthesized nanostructures. For example, we are interested in the idea of assembling (or self-assembling) such conductive polymer nanostructures into larger superstructures (e.g., grids, oriented films, or long wires). While the polycarbonate template membranes described here, can be dissolved by immersion in CH_2Cl_2 , the freed nanotubules quickly aggregate to form disordered mats. This precludes assembly of these nanostructures into a desired ordered superstructure.

If, upon dissolution of the membrane, the aggregation process could be prevented, sols of the template-synthesized nanostructures might be obtained. The individual nanostructures that make up such sols might then be assembled into the desired superstructures. Sols of template-synthesized Au nanoparticles have recently been obtained by dissolving the template membrane (in this case a microporous Al_2O_3), and dispersing the Au nanoparticles by ultrasonication in the presence of the dispersing agent, poly(vinylpyrrolidone) (3). In this report we describe a method for preparing sols of isolated template-synthesized polypyrrole nanotubules. This method uses an anionic surfactant (diamyl sulfosuccinate) as the dispersing agent.

Pyrrole (TCI 99%) was twice distilled under argon and stored only briefly at - 20° C prior to use. All solutions were made from purified water obtained by passing house distilled water through a Milli-Q (Millipore) water purification system. Ferric chloride hexahydrate (Aldrich), p-toluenesulfonic acid monohydrate (Aldrich), and diamyl 2-sodium sulfosuccinate (Fisher) were used as received. Poretics microporous polycarbonate filters (Osmonics) were used as the template membranes. Membranes with nominal pore diameters of 50 nm (6×10^8 pores cm^{-2}) and 200 nm (7×10^7 pores cm^{-2}) were used. The diameters of the polypyrrole tubules prepared in these membranes were larger than these nominal pore diameters (Table I).

The desired template membrane was immersed into an aqueous solution of pyrrole (0.2 M) at 0° C, and an equal volume of an aqueous solution that was 0.5 M in FeCl_3 and 0.5 M in p-toluenesulfonic acid (also at 0° C) was added. This resulted in oxidative polymerization of the pyrrole monomer within the pores and on the faces of the template membrane; a polymerization time of 1 hr was used. No effort was made to exclude O_2 during polymerization. After polymerization, the membrane was washed with water, and the polypyrrole surface films that coated both faces of the membrane were removed by polishing with a methanol-wetted laboratory tissue. Polypyrrole nanotubules synthesized in the nominally 50 nm and 200 nm pore-diameter membranes are referred to as PPy-50 and PPy-200 tubules, respectively.

After removal of the polypyrrole surface films, a $\sim 10 \text{ cm}^2$ piece of the polycarbonate membrane containing the polypyrrole tubules was immersed into 10 mL of absolute ethanol containing 1% by weight of diamyl sulfosuccinate. The membrane was exposed to this surfactant solution for three hours. Ten mL of CH_2Cl_2 were then slowly added to the surfactant solution by running this solvent down the glass wall of the beaker. In the absence of the anionic

surfactant this would result in rapid dissolution of the polycarbonate membrane. In the presence of this surfactant, the membrane softens but does not dissolve. Slowing down the dissolution of the template membrane is a critical factor in preventing aggregation of the polypyrrole nanotubules. This is undoubtedly because slow dissolution allows the surfactant time to adsorb to the polypyrrole tubule surfaces and because slow dissolution minimizes turbulence which promotes mixing and aggregation. After three hours, 50 mL of CH_2Cl_2 and 10 mL of the ethanol/surfactant solution were added. After an additional 5 min, the mixture was ultrasonicated for 3 hr to completely dissolve the template membrane. A dark colored sol was obtained.

Transmission electron microscopic (TEM) images of the polypyrrole tubules were obtained as follows: a piece of the tubule-containing membrane was placed on a copper TEM grid and CH_2Cl_2 was applied to dissolve the membrane. The tubules deposit on the grid. Such TEM images were used to measure the diameter and the wall thickness of the tubules. All TEM images were obtained using a JEOL 2000 scope (accelerating voltage of 100 kV).

Scanning electron microscopic (SEM) images of the polypyrrole sol were obtained using a Phillips 505 microscope (20 kV accelerating voltage). Samples were prepared as follows: a drop of the sol was placed onto a copper transmission electron microscopy grid (Ted Pella), and the solvent was allowed to evaporate. The resulting solid residue was washed with CH_2Cl_2 and then sputtered with 12 nm of Au to prevent charging during SEM imaging. Note that the SEM images were obtained after evaporation of the solvent from the polypyrrole nanotubule sol. This is important because if aggregation of the nanotubules is observed in such SEM images, it is not possible to ascertain whether these aggregates were present in the sol or whether aggregation occurred during removal of the solvent. A freeze-fracture TEM method was

used to explore this critical issue. This method entails quickly freezing a drop of the sol, fracturing the frozen drop, and imaging the fractured surface using TEM.

A copper freeze fracture sample holder was cooled to liquid nitrogen temperature by immersion into liquid N₂. A drop of the nanotubule sol was applied to the precooled sample holder which was then immediately re-immersed into liquid N₂. The cold sample was inserted into a freeze-fracture device (JEOL JFD9010C) in which pressure and temperature were maintained such that both condensation and evaporation could not occur ($T = -181^{\circ}\text{C}$, $P = 9 \times 10^{-6}\text{ Pa}$). The frozen drop was fractured with a cold ($T = -167^{\circ}\text{C}$) steel knife. The cleaved surface was immediately sputtered with Pt (15 nm) and then with carbon (150 nm) to make a replica of this surface. The Pt and C were deposited at an angle of 45° to shadow any nanostructures protruding from the cleaved surface. The sample was then removed from the freeze-fracture device and brought to room temperature. This resulted in liquefaction of the sol drop. The Pt-C replica of the cleaved surface was then washed with CH₂Cl₂ and placed on a Au TEM grid (Ted Pella).

Dissolution of the template membrane in the absence of the anionic surfactant results in clumping of the freed polypyrrole nanotubules, and these clumps quickly settled. When the anionic surfactant is used as described above, a fraction of the sample still clumps and settles; however, the remainder of the sample remains suspended, resulting in a dark colored sol. The fraction that remains suspended is higher for the PPy-50 tubules (~10-30 % of the sample) than for the PPy-200 tubules (~3-10% of the sample). The sols obtained are not, however, infinitely stable. The PPy-50 sols were observed to settle after several days of storage at room temperature. The PPy-200 sols began to settle after ~12 hours of storage.

SEM and TEM images in Figures 1-3 clearly show the template-synthesized polypyrrole nanotubules. As noted above, the diameter of the tubules is larger than the nominal membrane pore diameter (Table 1). The PPy-200 tubules are all 10 μm long, which is equivalent to the thickness of the template membrane. This indicates that the ultrasonication procedure used to dissolve the membrane does not damage these larger tubules. The PPy-50 tubules are often shorter than the thickness of the membrane suggesting damage during ultrasonication.

The SEM images in Figures 1 and 2 show some overlapping (i.e. aggregated) tubules, and as noted above, it is impossible to ascertain whether this aggregation occurred during evaporation of the solvent. It is important to point out, however, that these images of the sol fraction are very different from the images of the fraction of the tubules that clumped together, after membrane dissolution, and precipitation from the sol. As shown in Figure 4A, the PPy-50 tubules clump together in randomly arranged mats. Interestingly, the PPy-200 tubules clump together in ordered arrays (Figure 4B) One factor leading to such ordered arrays of the PPy-200 tubules is the greater stiffness of these larger diameter tubules.

The freeze-fracture TEM method was used to determine if aggregates are present in the sol. Figure 5 shows three representative images of the Pt-C replica of the freeze-fractured surface obtained from PPy-50 sols. Single (i.e., non-aggregated) PPy-50 tubules can be seen protruding from the surface of the fracture. Numerous images of this type were obtained and analyzed and in no cases were aggregated tubules seen. These results strongly suggest that the fraction of the sample remaining in suspension, when the anionic surfactant is used as the dispersing agent, is present as individual nanotubules. Our goal

now is to use these suspensions to assemble superstructures from these nanotubules.

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Table I. Characteristics of the Polypyrrole Nanotubules Obtained.

Nominal Pore Diameter (nm)	Measured Tubule Diameter (nm) ^a	Tubule Wall Thickness (nm) ^a	Tubule Length (μm)
50	110±20	42±7	3 to 7 ^b
200	250±50	50±10	10 ^b

^aObtained from transmission electron microscopic images.

^bThe thickness of the template membrane used.

Figure Captions.

Figure 1. Scanning electron micrographs of PPy-200 sol.

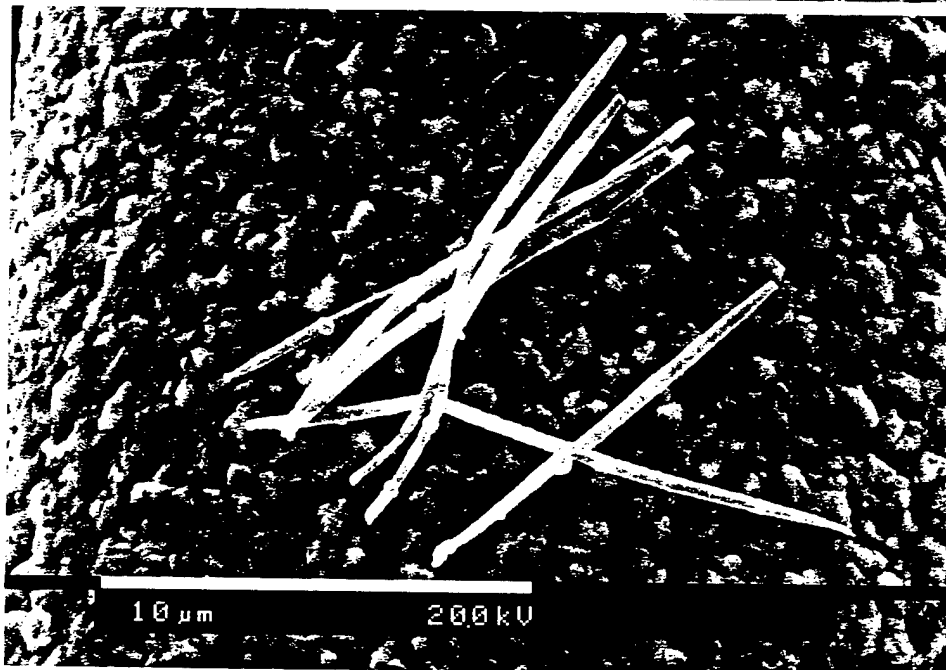
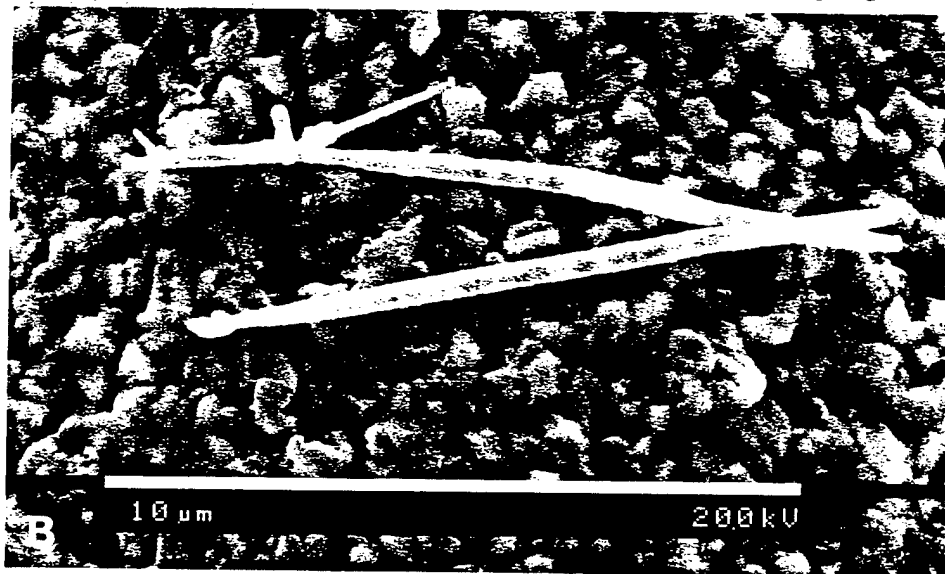
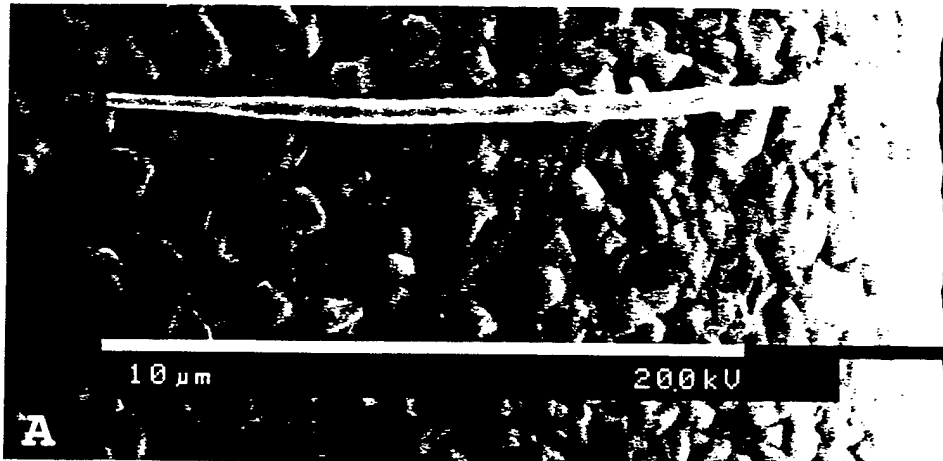
Figure 2. Scanning electron micrograph of PPy-50 sol.

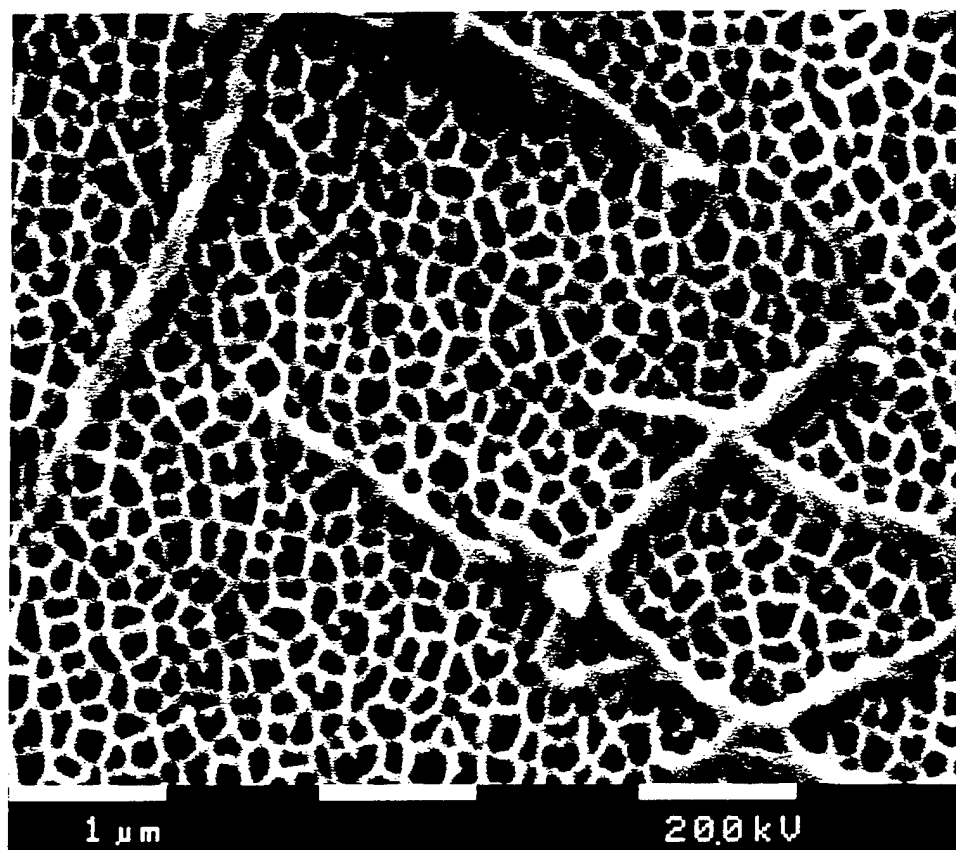
Figure 3. Transmission electron micrograph of PPy-200 tubules.

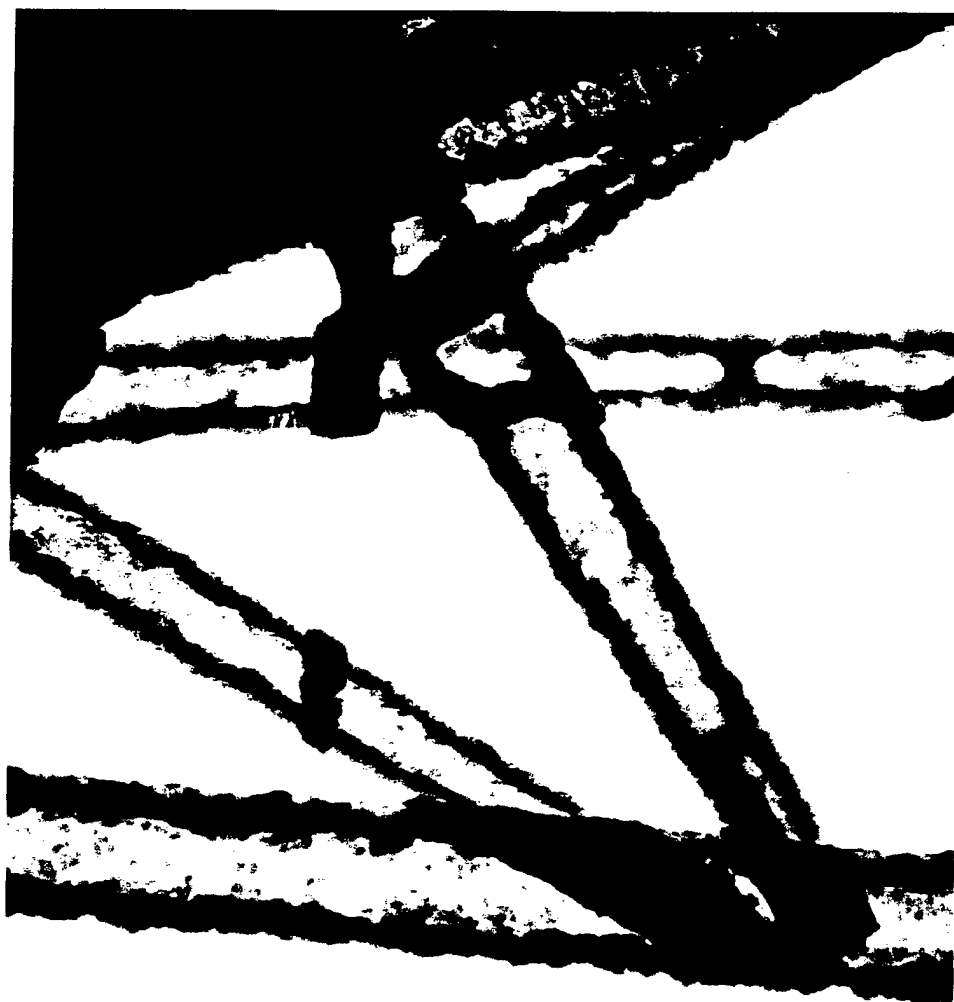
Figure 4A. Scanning electron micrograph of PPy-50 tubules precipitated in clumps from the sol.

Figure 4B. Scanning electron micrograph of PPy-200 tubules precipitated in ordered array from the sol.

Figure 5. TEM images of the Pt-C replicas obtained from freeze-fractured PPy-50 sol.







100.0KV X40K 200nm

